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# Emission spectra of $\text{Rb}^*\text{He}_n$ exciplexes in a cold $^4\text{He}$ gas

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We report on the systematic observation of emission spectra of  $\text{Rb}^*\text{He}_n$  exciplexes ( $n = 1, 2, \dots, 6$ ), realized by exciting Rb atoms to the  $5^2P$  states ( $\text{Rb}^*$ ) in a cold  $^4\text{He}$  gas. The observed broad spectral components are assigned to  $\text{Rb}^*\text{He}_n$  ( $n = 1-6$ ) using theoretical spectra obtained from *ab initio* potential curves. The dynamics of the exciplex formation is discussed, based on the observed temperature dependence of the spectra. The He gas density dependence of the spectra of  $\text{Rb}^*\text{He}$  is understood as a change in the population distribution over the vibrational levels. The present results are compared with our previous work with Cs [K. Enomoto *et al.*, Phys. Rev. A **66**, 042505 (2002)], and differences are explained in terms of the difference in the fine-structure splitting. Furthermore, we show the emission spectrum observed after the excitation of Rb in liquid He and conclude that it is the fluorescence from the exciplex  $\text{Rb}^*\text{He}_6$ .

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## I. INTRODUCTION

Alkali-metal atoms excited to the first  $P$  states in a cold He environment produce alkali-metal- $\text{He}_n$  exciplexes. The exciplex formation was discussed in order to give an explanation on the fact that the  $D$  emission lines were not observed from excited light alkali-metal atoms (Li, Na, K) in liquid He [1,2]. Kanorsky *et al.* and Dupont-Roc have proposed a model that several He atoms are localized at the place where the valence electron density of the alkali-metal atom is small [3,4]. Dupont-Roc paid attention to the spin-orbit coupling in the  $P$  state of alkali-metal atoms, and dealt with two typical cases, Cs and Na [4]. He discussed separately two fine structure components of Cs ( $6^2P_{3/2}$  and  $6^2P_{1/2}$ ), based on the fact that the fine-structure splitting  $\Delta$  of the  $6^2P$  states ( $554.0 \text{ cm}^{-1}$ ) is large compared to the splitting induced by an interaction with liquid He. He pointed out that the valence electron of Cs( $6^2P_{3/2}$ ) holds the applelike density distribution and only two He atoms can stick to the Cs core along the nodal line. On the other hand, due to the small fine-structure splitting, the orbital of the valence electron of Na is well expressed by a  $p_z$  orbital, and five or six He atoms are localized on a ring on the nodal plane of the valence electron orbital.

In our previous studies of Rb in the  $5^2P$  states (hereafter simply written as  $\text{Rb}^*$ ) in superfluid  $^4\text{He}$ , pressure-dependent quenching of the  $D_1$  emission line ( $5^2P_{1/2} \rightarrow 5^2S_{1/2}$ ) was observed [5]. This phenomenon is considered to be due to the pressure dependent decay process from the  $5^2P_{1/2}$  state to the exciplex  $\text{Rb}^*\text{He}_n$  which may emit infrared fluorescence. The  $\text{Rb}^*\text{He}_n$  exciplex was predicted to have the  $\text{Na}^*\text{He}_n$ -type configuration, that is,  $n$  He atoms form a ring around  $\text{Rb}^*$ , since no emission line was observed at the spectral region where the emission from  $\text{Rb}^*\text{He}_2$  is expected to be seen. The number  $n$  of He atoms was roughly estimated to be about six under the assumption that the distance between neighboring He atoms is equal to

that in liquid He [5]. We searched for the emission spectrum of  $\text{Rb}^*\text{He}_n$  in liquid He over an infrared region and found a broad emission band with a peak at  $7000 \text{ cm}^{-1}$ . This experimental result will be briefly presented in this paper. This band was the only spectrum of exciplex we could observe, and emission from smaller exciplexes was absent. The absence of the emission from smaller exciplexes indicates that the formation rates of exciplexes in liquid He are much faster than their radiative decay rates due to the high atom density of liquid He, and only the terminal exciplex is observed in liquid He. In the following, we will write the number of He atoms in the exciplex observed in liquid He as  $n_{\text{max}}$ . If the emission spectra of the intermediate exciplexes  $\text{Rb}^*\text{He}_n$  ( $1 \leq n < n_{\text{max}}$ ) can be observed, the value of  $n_{\text{max}}$  may be determined accurately. Recently, Brühl *et al.* have observed the emission spectrum of  $\text{Rb}^*\text{He}$  detached from He droplets [6]. The spectra for  $2 \leq n < n_{\text{max}}$ , however, have not been observed so far.

The main purpose of this paper is to present the emission spectra of  $\text{Rb}^*\text{He}_n$  ( $n = 1, 2, \dots, n_{\text{max}}$ ) observed in a cold glass cell containing Rb atoms and a He gas. The He density in the cell is, in the present case, two orders of magnitude less than in liquid He, so that the formation rates of the exciplexes become comparable to their radiative decay rates, which enables us to observe the emission spectra of the intermediate exciplexes. Such an observation of the spectrum of intermediate exciplex was first made for Ag by Jakubek *et al.* [7]: they observed emission spectra of  $\text{Ag}^*\text{He}_n$  ( $n = 1, 2$ ) in a cold He gas, although the emission from  $n = 1$  was absent in liquid He [8]. We recently reported emission spectra of  $\text{Cs}^*\text{He}_n$  ( $n = 1, 2$ ) [9]. The spectrum of  $\text{Cs}^*\text{He}$ , which was also absent in liquid He, could be observed by the use of the He gas environment.

Another interest of the present work concerns the dynamics of the exciplex formation ( $\text{Rb}^* \rightarrow \text{Rb}^*\text{He} \rightarrow \dots \rightarrow \text{Rb}^*\text{He}_{n_{\text{max}}}$ ). We investigate the dynamics by observing the temperature dependence of the emission spectra. It should be mentioned that, in the present experiment, the temperature and the He density can be changed over a wide range, which is in contrast to experiments with liquid He or

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He droplets. This helps us to study not only the dynamics of the exciplex formation but also the dynamics of relaxation processes induced by collisions with He atoms. In the present work, we evaluate the rate coefficient for the fine-structure relaxation of Rb\*He.

We are also interested in comparing the results of the present work and our previous experiment with Cs [9]. A remarkable difference is that Rb has larger  $n_{max}$  than Cs ( $n_{max}=2$ ). The spin-orbit coupling strength should concern this difference and a quantitative study on the influence of the spin-orbit interaction is needed to explain the difference in  $n_{max}$  between Rb and Cs, since the splitting  $\Delta$  of Cs is on the same order of magnitude as that of the Rb-5<sup>2</sup>P states (237.6 cm<sup>-1</sup>) and the difference in potential energy between the pairs Cs\*-He and Rb\*-He is not so large (see, for example, potentials in Ref. [10]). Thus, in the present work, we calculate potential-energy surfaces for the systems Rb\*He<sub>2</sub>-He and Cs\*He<sub>2</sub>-He taking into account the spin-orbit interaction, and consider the difference in the formation of  $n=3$ .

The paper is organized as follows. In Sec. II, we show theoretical emission spectra of Rb\*He<sub>n</sub> calculated from *ab initio* potential curves. In Sec. III, we describe the experimental method. In Sec. IV, we first present the experimental results (Sec. IV A), and assign the observed spectra (Sec. IV B). Next, we describe the temperature dependence of the spectra (Sec. IV C), with which we discuss the dynamics of the exciplex formation (Sec. IV D). We also show analysis on the He gas density dependence of the spectra of Rb\*He (Sec. IV E). Finally, we discuss differences between the results for Rb and Cs (Sec. IV F).

## II. THEORETICAL EMISSION SPECTRA

We calculated theoretical emission spectra of Rb\*He<sub>n</sub> ( $n=1-7$ ). With respect to the potential energies of Rb\*He<sub>n</sub>, we carried out *ab initio* calculations with the MOLPRO program package [11], using the 3-21G\* basis set [12] for the Rb atom and the 6-31G\*\* basis set [13] for the He atoms.

To obtain emission spectra of Rb\*He, we first calculated potential curves of the lowest two <sup>2</sup>Σ and one <sup>2</sup>Π states of Rb\*He. At each value of internuclear distance  $r$ , energies of the three states were calculated by a sequence of the restricted Hartree-Fock (RHF) calculation, the multiconfiguration self-consistent field calculation [14], and the internally contracted multireference configuration interaction calculation [15]. With respect to the potential energies of the excited states, we took into account the spin-orbit interaction of the Rb-5<sup>2</sup>P states ( $\Delta=237.6$  cm<sup>-1</sup>), based on the assumption that it is independent of the internuclear distance  $r$  [16]. We consider that this assumption is quite valid for Rb\*He<sub>n</sub>. To the best of our knowledge, there is no study on the fine-structure of a Rb-rare-gas exciplex or complex. There are, however, several studies on the complex of Na and a heavy rare-gas atom (Ar, Kr, Xe) [17–20]. According to these studies, with decreasing the mass of rare-gas atoms, i.e., decreasing the polarizability, the fine-structure splitting of the Na-rare-gas complexes comes close to the value expected from

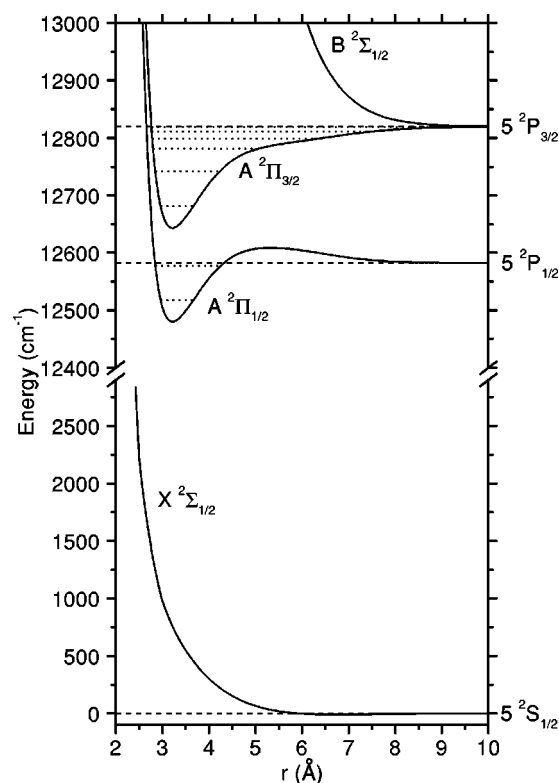


FIG. 1. Theoretical Rb-He potential curves of the ground state ( $X^2\Sigma_{1/2}$ ) and the excited states ( $A^2\Pi_{1/2}$ ,  $A^2\Pi_{3/2}$ , and  $B^2\Sigma_{1/2}$ ) obtained from *ab initio* calculations. Dotted lines show the vibrational energy levels (see also Table I). Asymptotic energies of the potentials are shown by dashed lines, which are labeled on the right-hand side by atomic states of Rb.

this assumption, which is  $\frac{2}{3}\Delta$  in Hund's case (a). The deviation from the assumption is less than  $\sim 30\%$  even for Ar [17,18], so it is natural to consider that the deviation for He should be much smaller than that for Ar because of the small polarizability of He which is about eight times smaller than that of Ar [21]. The potential curves of the excited states were shifted so that they coincided with the energy levels of Rb + He in the  $r \rightarrow \infty$  limit. Figure 1 shows the potential curves obtained for the ground state  $X^2\Sigma_{1/2}$  and the excited states  $A^2\Pi_{1/2}$ ,  $A^2\Pi_{3/2}$ , and  $B^2\Sigma_{1/2}$ . The repulsive  $B^2\Sigma_{1/2}$  and attractive  $A^2\Pi_{3/2}$  states correlate to the asymptotic state Rb( $5^2P_{3/2}$ ) + He. The  $A^2\Pi_{3/2}$  potential has the minimum at  $r=3.21$  Å with a depth of 176.8 cm<sup>-1</sup> below the dissociation limit. The potential of the  $A^2\Pi_{1/2}$  state correlating to Rb( $5^2P_{1/2}$ ) + He also has the minimum at  $r=3.21$  Å with a depth of 102.1 cm<sup>-1</sup> below the dissociation limit. The  $A^2\Pi_{1/2}$  potential exhibits a potential barrier at  $r=5.3$  Å with a height of 26.5 cm<sup>-1</sup> above the dissociation limit. This barrier would prevent the entrance of the He atom into the potential well, when the Rb atom is excited to the  $5^2P_{1/2}$  state at about liquid He temperatures.

With the help of the BCONT 2.0 program code [22], we numerically calculated the vibrational wave function  $\psi'(r)$  for the excited states  $A^2\Pi_{1/2}$  and  $A^2\Pi_{3/2}$ , and then calculated emission spectra  $I(\nu)$  for the transitions from the obtained vibrational levels to the ground state  $X^2\Sigma_{1/2}$  using the

EMISSION SPECTRA OF  $\text{Rb}^*\text{He}_n$  EXCIPLEXES IN A . . .

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TABLE I. Vibrational levels in the  $A^2\Pi_{3/2}$  and  $A^2\Pi_{1/2}$  states of  $\text{Rb}^*\text{He}$ . The energies are given relative to the dissociation limits  $\text{Rb}(5^2P_{3/2}) + \text{He}$  and  $\text{Rb}(5^2P_{1/2}) + \text{He}$ , respectively.

|                | Vibrational level | Energy ( $\text{cm}^{-1}$ ) |
|----------------|-------------------|-----------------------------|
| $A^2\Pi_{3/2}$ | $v=5$             | -1.1                        |
|                | $v=4$             | -9.0                        |
|                | $v=3$             | -20.9                       |
|                | $v=2$             | -39.1                       |
|                | $v=1$             | -78.3                       |
|                | $v=0$             | -138.8                      |
| $A^2\Pi_{1/2}$ | $v=1$             | -5.2                        |
|                | $v=0$             | -64.4                       |

relation  $I(\nu) \propto \nu^3 |\int \psi'(r) \psi(r; \nu) dr|^2$ , where  $\psi(r; \nu)$  is the continuum wave function for the repulsive  $X^2\Sigma_{1/2}$  state and  $\nu$  is the transition frequency. Table I shows the calculated energies of the vibrational levels. The states  $A^2\Pi_{3/2}$  and  $A^2\Pi_{1/2}$  have six and two levels, respectively. Figure 2 shows the calculated emission spectrum for each vibrational level. Here we have assumed that the transition dipole moment of  $\text{Rb}^*\text{He}$  is equal to that of  $\text{Rb}$ . With the *ab initio* calculation, we confirmed that the transition moment changes only 3% in the range  $r > 2.5 \text{ \AA}$ .

We obtained emission spectra also from Pascale's  $\text{Rb-He}$  potential curves [10], taking into account the spin-orbit in-

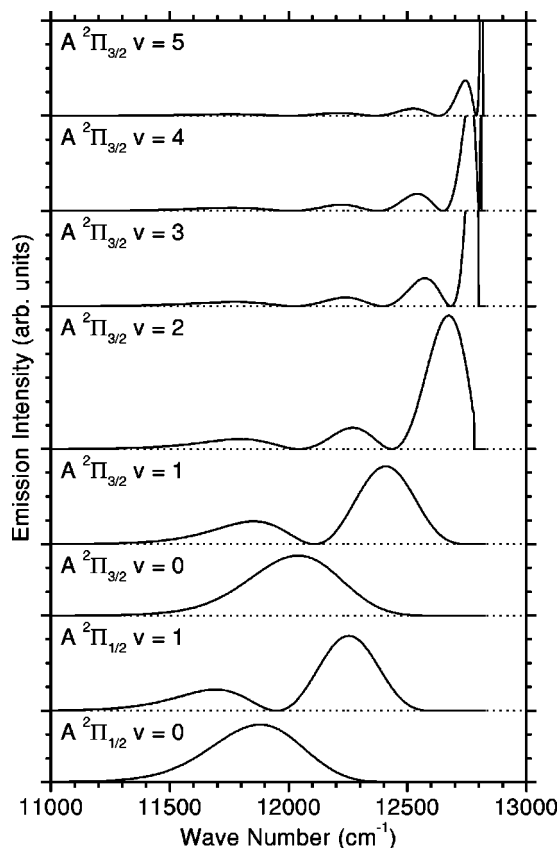


FIG. 2. Theoretical emission spectra from the vibrational levels of  $\text{Rb}^*\text{He}$ .

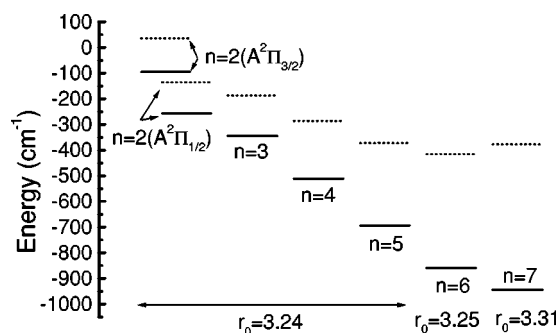


FIG. 3. Potential energy  $E'_n$  at the bottom of the potential well (solid lines) and the energy level  $E_n$  of the vibrational ground state (dotted lines) in the first electronic excited state for each  $n$ . The equilibrium radius  $r_0$  in units of  $\text{\AA}$  is also shown.

teraction. However, the results were found to be in worse agreement with experimental spectra than the spectra obtained from the *ab initio* potentials: the peak position of the emission spectrum from the  $A^2\Pi_{1/2} v=0$  state was calculated to be  $11880 \text{ cm}^{-1}$  and  $12018 \text{ cm}^{-1}$  from the *ab initio* and Pascale's potentials, respectively, whereas the peak was observed at  $11820 \text{ cm}^{-1}$  as shown later.

We calculated emission spectra of  $\text{Rb}^*\text{He}_n$  ( $n=2-7$ ) under the assumption that  $n$  He atoms are located equidistantly on a circle with the center at the position of  $\text{Rb}$ . We calculated at the RHF level *ab initio*  $\text{Rb-He}_n$  potential curves as functions of the radius  $r$  of the circle [11], and took into account the spin-orbit interaction [16]. The equilibrium radius  $r_0$  obtained for each potential curve is shown in Fig. 3. It should be noted that, for  $n=2$ , the lowest two of the three excited states ( $A^2\Pi_{1/2}$  and  $A^2\Pi_{3/2}$ ) have attractive potentials, whereas for  $n \geq 3$ , only the lowest state has attractive potential.

For  $n \geq 3$ , the energy difference between the lowest two excited states before the consideration of the spin-orbit interaction is larger than  $10\Delta$  at  $r=r_0$ . As a result, with respect to the lowest excited state, more than 99% of the  $\text{Rb}$  valence electron occupies the  $p_z$  orbital which has the  $z$  axis along the axis of the circle, even after the spin-orbit interaction is considered. So it can be said that the spin-orbit coupling is substantially decoupled for  $n \geq 3$ .

For each potential curve obtained for the attractive electronic state of  $\text{Rb}^*\text{He}_n$ , we calculated the energy of the vibrational ground state, and obtained emission spectrum from the state. The calculation procedure is as follows. First we calculated the vibrational wave function  $\psi'_{\text{sym}}(r)$  for the symmetric vibration mode, which originates from the variation of  $r$ , and a function  $I'(\nu) \propto \nu^3 |\int \psi'_{\text{sym}}(r) \psi_{\text{sym}}(r; \nu) dr|^2$  with the help of the BCONT 2.0 program [22], where  $\psi_{\text{sym}}(r; \nu)$  is the continuum wave function for the symmetric motion in the electronic ground state. In addition, taking into account all vibrational modes, we calculated at the RHF level the sum  $\epsilon$  of the zero-point energies for all the other vibrational modes [11,23]. The spin-orbit coupling was neglected in the calculation of  $\epsilon$  for  $n=3-7$ , because it is substantially decoupled as mentioned above. Then we approximated the emission spectrum as

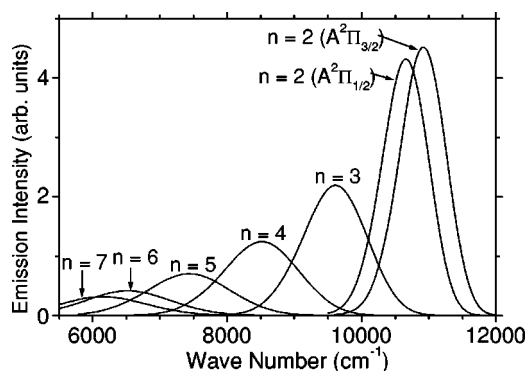


FIG. 4. Theoretical emission spectrum of  $\text{Rb}^*\text{He}_n$  ( $n=2-7$ ) calculated for the transition from the vibrational ground state. For  $n=2$ , initial electronic state is indicated in parentheses.

$I'(\nu - \epsilon)$ , that is, the function  $I'(\nu)$  was shifted toward larger wave number by the amount of  $\epsilon$ . The calculated emission spectra are shown in Fig. 4, where we see that the emission spectrum exhibits a redshift, broadening, and a decrease in the integrated intensity, as  $n$  increases. The redshift is mainly due to the increase in the repulsive energy of the ground state. The broadening is attributed to the increase in the slope of the repulsive wall of the ground-state potential. The emission intensity becomes weak as the transition energy  $\nu$  is decreased, because the radiative transition rate is proportional to  $\nu^3$ .

We show in Fig. 3 the potential energy  $E'_n$  at the bottom of the potential well and the energy  $E_n$  of the vibrational ground state, for each exciplex. The value  $E_n - E'_n$  corresponds to the total zero-point energy. Let us consider here the maximum number of sticking He atoms,  $n_{\max}$ . We consider that the number  $n_{\max}$  is the maximum value of  $n$  satisfying the relation  $\Delta E_n = E_{n-1} - E_n > 0$ . The energy differences are obtained as  $\Delta E_4 = 99.5 \text{ cm}^{-1}$ ,  $\Delta E_5 = 85.8 \text{ cm}^{-1}$ ,  $\Delta E_6 = 43.9 \text{ cm}^{-1}$ , and  $\Delta E_7 = -38.7 \text{ cm}^{-1}$ . Therefore, it is suggested from this theoretical consideration that the number  $n_{\max}$  is 6.

### III. EXPERIMENTAL SETUP AND PROCEDURE

The experimental setup is illustrated in Fig. 5(a). A Pyrex glass cell (cubic:  $2 \times 2 \times 2 \text{ cm}^3$ ) containing a small amount of Rb metal was mounted in a pumped liquid He cryostat with optical glass windows. The cell was filled with 730 torr  $^4\text{He}$  gas at the liquid  $\text{N}_2$  temperature (77 K) and was sealed. The cell temperature  $T$  was varied from about 1.3 K to room temperature, and it was monitored with a calibrated sensor placed near the cell. The He gas density in the cell is constant ( $9 \times 10^{19} \text{ cm}^{-3}$ ) above the condensation temperature  $T_c = 1.9 \text{ K}$ , whereas it decreases as  $T$  falls below  $T_c$ , following the saturated vapor pressure of He [see Fig. 5(b)]. Gaseous Rb atoms in the cryogenic cell were produced with the laser ablation method, in which the second harmonic of a Q-switched Nd:YLF<sub>4</sub> (YLF) laser (wavelength 523 nm, repetition rate 1 kHz, and pulse energy 100  $\mu\text{J}$ ) was focused on a small area of the cell wall covered with a thin film or small particles of Rb. Within a few seconds, we obtained a Rb

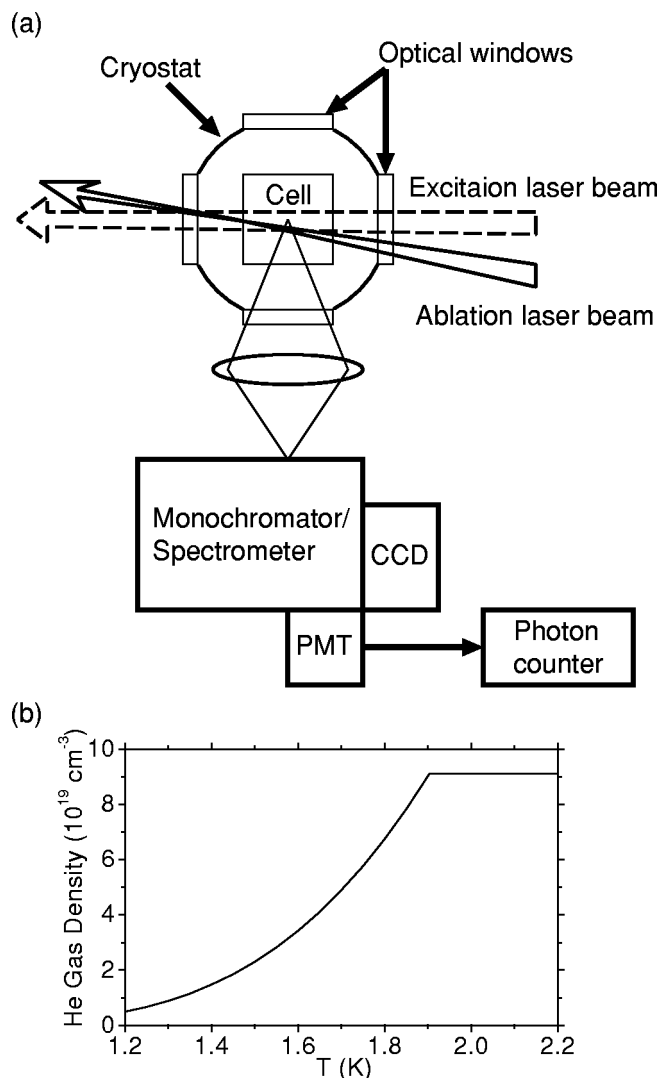


FIG. 5. (a) Experimental setup. (b) He gas density in the cell as a function of  $T$ .

vapor at a density of  $10^8 - 10^{10} \text{ cm}^{-3}$ . Details of our cryostat system and the procedure of preparing the cell have been reported already [24]. In the present work, we did not use the light-induced atom desorption method reported in Ref. [24], since it is not effective in producing alkali-metal vapors at  $T > T_c$ .

The Rb atoms produced in this way were excited with a diode laser through either the  $D_2$  transition ( $5^2S_{1/2} \rightarrow 5^2P_{3/2}$ ,  $12820 \text{ cm}^{-1}$ ) or the  $D_1$  transition ( $5^2S_{1/2} \rightarrow 5^2P_{1/2}$ ,  $12582 \text{ cm}^{-1}$ ). The typical intensity of the diode laser beam was  $0.2 \text{ W/cm}^2$  in front of the cell. The fluorescence introduced to a monochromator was detected with an infrared-sensitive photomultiplier tube (PMT) (Hamamatsu, R5509-71) and a photon counter. The PMT has sufficient sensitivity in the wave number range down to about  $6000 \text{ cm}^{-1}$ . The spectral resolution of our monochromator-PMT system was  $\approx 150 \text{ cm}^{-1}$ . To obtain higher resolution for the spectral range down to about  $10000 \text{ cm}^{-1}$ , we introduced the fluorescence to a spectrometer and detected with a charge-coupled-device (CCD) (Princeton instruments, LN/



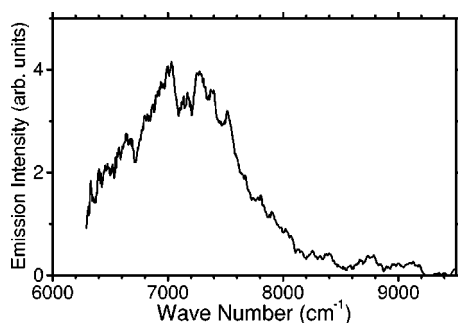


FIG. 6. Emission spectrum of  $\text{Rb}^*\text{He}_{n_{\max}}$  in liquid He.

CCD-1100PF). This spectrometer-CCD system measures a wide-ranging spectrum ( $\geq 2000 \text{ cm}^{-1}$ ) at once, without the influence of fluctuation of the Rb vapor density. Therefore, we could obtain a better signal to noise ratio with higher resolution of about  $20 \text{ cm}^{-1}$ , than in the case of the monochromator-PMT system. The detection systems have been calibrated with a commercial standard lamp. All the measured spectra have been normalized by the emission intensity integrated over the measured spectral range.

In this paper, we also present an emission spectrum of  $\text{Rb}^*\text{He}_n$  in liquid He observed in an infrared region. The experimental setup for the observation of this spectrum was almost the same as that of Ref. [25]. Rb metal immersed in superfluid liquid He at the temperature of 1.88 K was ablated with the YLF pulse laser. Rb atoms isolated in liquid He were excited by a cw  $\text{Ti}:\text{Al}_2\text{O}_3$  laser beam tuned to the  $D_2$  line (wave number  $13\,072 \text{ cm}^{-1}$ ). With a dark period of  $50 \mu\text{s}$  for thermalization after each ablation pulse, the fluorescence from  $\text{Rb}^*\text{He}_n$  was detected with the PMT and the photon counting system.

## IV. RESULTS AND DISCUSSION

### A. Overview of experimental results

At first, we show the emission spectrum of  $\text{Rb}^*\text{He}_n$  in liquid He in Fig. 6. In addition to this infrared emission, the  $D_1$  emission line of  $\text{Rb}^*$  is observed at about  $12\,600 \text{ cm}^{-1}$  in liquid He [25]. This broadband infrared spectral component peaks at about  $7100 \text{ cm}^{-1}$  and has a full width at half maximum (FWHM) of about  $1230 \text{ cm}^{-1}$ . This is the emission spectrum from the terminal exciplex  $\text{Rb}^*\text{He}_{n_{\max}}$ . It is important to note that there is no other spectral component between this broadband component and the  $D_1$  emission line.

The emission spectra of  $\text{Rb}^*\text{He}_n$  observed in cryogenic gaseous He are shown in Figs. 7(a) and 7(b) in the cases of the  $D_2$  and  $D_1$  excitations, respectively. They were observed with the monochromator-PMT system. The observed spectra consist of several broad spectral components in addition to the sharp  $D$  lines of Rb. These components are assigned to the emission from  $\text{Rb}^*\text{He}_n$ , as described in detail in Sec. IV B. With respect to the peak positions or widths of the components, difference cannot be seen between the spectra for the  $D_2$  and  $D_1$  excitations. Particularly for the two components at about  $11\,800 \text{ cm}^{-1}$  and  $10\,800 \text{ cm}^{-1}$ , we con-

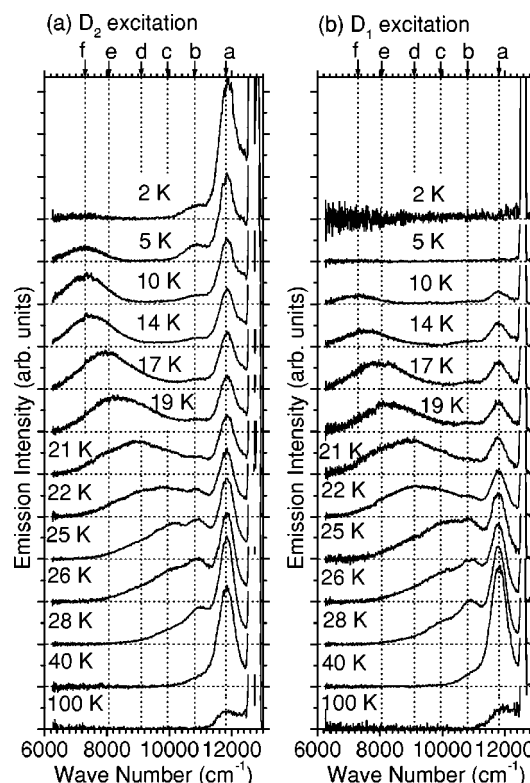


FIG. 7. Emission spectra observed in the cases of the  $D_2$  excitation (a) and  $D_1$  excitation (b) at different temperatures. Vertical dotted lines labeled as a–f indicate experimentally obtained peak positions of spectral components for  $\text{Rb}^*\text{He}_n$  ( $n=1-6$ ). They are located at  $11\,820 \text{ cm}^{-1}$ ,  $10\,810 \text{ cm}^{-1}$ ,  $9\,949 \text{ cm}^{-1}$ ,  $9\,105 \text{ cm}^{-1}$ ,  $8\,065 \text{ cm}^{-1}$ , and  $7\,300 \text{ cm}^{-1}$ , respectively (see Sec. IV B).

firmed this by measuring better resolved spectra with the spectrometer-CCD system. We found in this measurement that the former had a peak at  $11\,820 \text{ cm}^{-1}$  and the FWHM of  $610 \text{ cm}^{-1}$  and the latter  $10\,810 \text{ cm}^{-1}$  and  $670 \text{ cm}^{-1}$ , respectively.

He gas density in the cell is constant ( $9 \times 10^{19} \text{ cm}^{-3}$ ) in the temperature range  $T \geq 2 \text{ K}$  shown in Figs. 7(a) and 7(b). Nevertheless, the emission spectra observed are strongly dependent on  $T$ . In Fig. 7(b) showing the result of the  $D_1$  excitation, no spectral components except the  $D_1$  emission line can be observed at  $T \leq 5 \text{ K}$ , but broad components of  $\text{Rb}^*\text{He}_n$  appear as  $T$  rises above  $5 \text{ K}$ . This is different from the  $D_2$  excitation case, in which broad components can be seen even at  $T \leq 5 \text{ K}$ . Apart from this difference, the broad emission spectra in both cases of the  $D_2$  and  $D_1$  excitations are dependent on  $T$  in the same manner.

(1) The ratio of the integrated intensity of the emission from  $\text{Rb}^*\text{He}_n$  to the total emission intensity has a maximum of about 50% at  $T \approx 25 \text{ K}$ . The ratio decreases with increasing  $T$  above  $25 \text{ K}$ , and at  $100 \text{ K}$  it is about 6%.

(2) At  $T \leq 10 \text{ K}$ , the spectra consist mainly of the components at  $11\,820 \text{ cm}^{-1}$ ,  $10\,810 \text{ cm}^{-1}$ , and  $7\,300 \text{ cm}^{-1}$ . As  $T$  increases above  $10 \text{ K}$ , the broad spectrum at  $7\,300 \text{ cm}^{-1}$  seems to shift toward larger wave number, until it merges into the component at  $11\,820 \text{ cm}^{-1}$  at  $T \approx 40 \text{ K}$ .

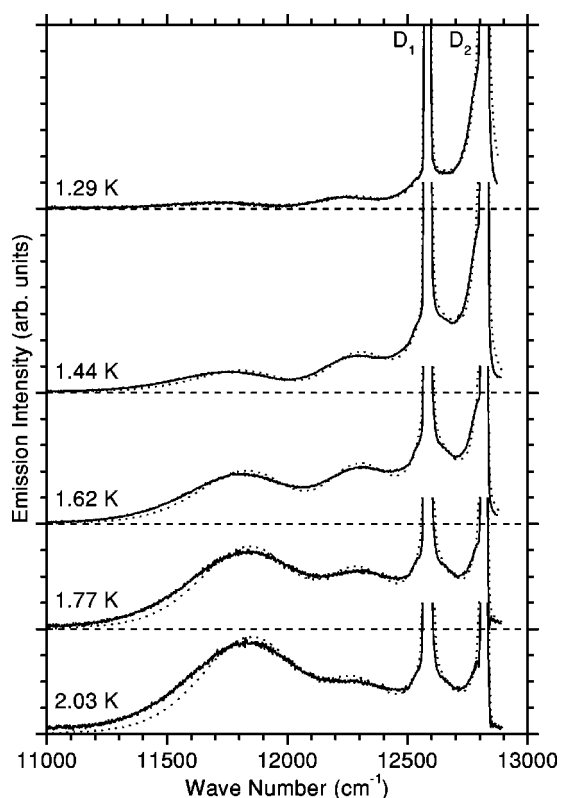


FIG. 8. Emission spectra observed in the case of the  $D_2$  excitation (solid lines). The dotted lines show the best-fitted curves, which are composed of the  $D_2$  and  $D_1$  lines of Rb and the theoretical emission spectra from the vibrational levels of  $\text{Rb}^*\text{He}$  shown in Fig. 2.

Figure 8 shows emission spectra measured at  $T < 2.1$  K in the case of the  $D_2$  excitation. These were measured with the spectrometer-CCD system. The observed spectra have structure resulting from the vibrational levels of  $\text{Rb}^*\text{He}$ , as described in Secs. IV B and IV E. Similar emission spectra were observed after the  $D_2$  excitation of Rb atoms on He droplets [6]. The spectral profile shown in Fig. 8 is strongly dependent on  $T$ , especially at  $T < T_c$  ( $= 1.9$  K), where the He gas density in the cell drastically changes with  $T$  as shown in Fig. 5(b). To distinguish the He gas density dependence from the temperature dependence, we measured emission spectra using another cell for which  $T_c = 1.7$  K. The observed spectra were nearly the same as the spectra shown in Fig. 8 at  $T \leq 1.7$  K, but were approximately independent of  $T$  for  $1.7 \text{ K} < T < 2.1$  K. Thus, it is concluded that the temperature dependence at  $T < T_c$  is caused by the change of the He gas density.

### B. Assignment of the observed spectra

We start with the component at  $11\,820 \text{ cm}^{-1}$  (FWHM  $= 610 \text{ cm}^{-1}$ ), which is seen over a wide temperature range [see Figs. 7(a) and 7(b)]. This component is assigned to the emission from the  $A^2\Pi_{1/2}v=0$  state of  $\text{Rb}^*\text{He}$ . As already mentioned in Sec. II, there are two attractive electronic states  $A^2\Pi_{3/2}$  and  $A^2\Pi_{1/2}$  for  $\text{Rb}^*\text{He}$  (and also for  $\text{Rb}^*\text{He}_2$ ). The reason why the component is assigned to the emission from

the  $A^2\Pi_{1/2}$  state is that it was observed in both cases of the  $D_2$  and  $D_1$  excitations. This discussion is based on the fact that in the case of the  $D_1$  excitation, the  $D_2$  emission line was not observed at  $T \leq 40$  K, implying that  $\text{Rb}^*\text{He}(A^2\Pi_{3/2})$  was not produced by collisional excitation of fine-structure transition. The assignment is supported by a good agreement between the wave number at peak and FWHM of the observed component and those of the calculated spectrum from the  $A^2\Pi_{1/2}v=0$  state;  $11\,880 \text{ cm}^{-1}$  and  $453 \text{ cm}^{-1}$ , respectively (see Fig. 2).

The spectra observed at  $T < 2.1$  K shown in Fig. 8 are considered to be superpositions of several components from the vibrational levels of  $\text{Rb}^*\text{He}$  (see Fig. 2). The He gas density dependence can be understood as a change in the population distribution over the vibrational levels, as described in detail in Sec. IV E. At a low value of the He gas density ( $T \leq 1.7$  K), we observed an emission spectrum in the wave number region between the  $D_2$  and the  $D_1$  lines (mainly on the red wing of the  $D_2$  line). This emission originates from the high vibrational levels ( $v \geq 2$ ) of the  $A^2\Pi_{3/2}$  state. As the He gas density increased, the spectrum at  $11\,820 \text{ cm}^{-1}$  originating from the  $A^2\Pi_{1/2}v=0$  state became dominant.

Among the components from the vibrational levels of  $\text{Rb}^*\text{He}$ , the component from the  $A^2\Pi_{1/2}v=0$  state was dominant also at  $T \geq 2$  K. It is natural to think that emission from  $\text{Rb}^*\text{He}_n$  ( $n \geq 2$ ) also has its origin mainly in the vibrational ground state at  $T \geq 2$  K. Our assignment in the following is based on this approximation. Thus, we compare the peak position of the observed spectral component, shown in Figs. 7(a) and 7(b), with that of theoretical spectrum from the vibrational ground state of  $\text{Rb}^*\text{He}_n$  ( $n \geq 2$ ), shown in Fig. 4.

The component at  $10\,810 \text{ cm}^{-1}$  is assigned to  $\text{Rb}^*\text{He}_2$  by comparison of the experimental and theoretical peak positions. This component was observed also in both cases of the  $D_2$  and  $D_1$  excitations, and thus is assigned to the emission from the  $A^2\Pi_{1/2}$  state, based on the same discussion as above.

Another component at about  $10\,000 \text{ cm}^{-1}$ , which is identified only at around 25 K, is assigned to  $\text{Rb}^*\text{He}_3$ . Difference between the observed and theoretical wave numbers at peak, however, is larger than in the cases of  $n = 1, 2$ .

The other clearly identified is a component at  $7300 \text{ cm}^{-1}$  and with FWHM of about  $1400 \text{ cm}^{-1}$ , which is seen at  $T \leq 10$  K. This component agrees well with the spectrum observed in liquid He shown in Fig. 6. Therefore, the component is the emission from  $\text{Rb}^*\text{He}_{n_{\text{max}}}$ .

The broad spectra with a peak in the wave number region from  $7300 \text{ cm}^{-1}$  to  $10\,000 \text{ cm}^{-1}$ , which were observed at  $10 \text{ K} < T < 25 \text{ K}$ , are superpositions of several components. The observed peak shift with  $T$  is due to a change in the relative intensities of the components. Since FWHM of each component is estimated to be, at most,  $1400 \text{ cm}^{-1}$  (the value for  $\text{Rb}^*\text{He}_{n_{\text{max}}}$ ), at least two components are required to exist between the spectra of  $\text{Rb}^*\text{He}_3$  and  $\text{Rb}^*\text{He}_{n_{\text{max}}}$  to explain the smooth peak shift. The difference spectrum between at 26 K and 28 K indicates the existence of a component at

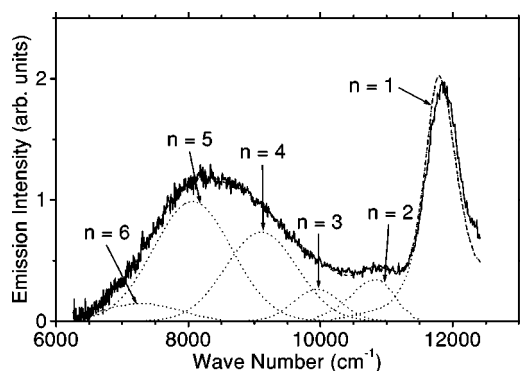


FIG. 9. Example of the fitting result. The solid line shows the spectrum observed at 19 K in the case of the  $D_2$  excitation. The atomic  $D$  lines, which were not considered in the fitting, have been removed from the spectrum. The best-fitted curve (dashed line) consists of the six components for  $\text{Rb}^*\text{He}_n$  ( $n=1-6$ ) (dotted lines). The three components for  $n=3-5$  are Gaussian functions determined by the fitting, and the other three for  $n=1,2,6$  are experimentally determined profiles which were used in the fitting.

about  $9000 \text{ cm}^{-1}$ , in the red tail of the  $\text{Rb}^*\text{He}_3$  component. The same component can be seen in the difference spectrum between at 17 K and 19 K. Similarly, the existence of a component at about  $8100 \text{ cm}^{-1}$  is indicated by comparing the spectrum at 14 K (21 K) with that at 10 K (22 K). We do not consider that there exists another component besides the two components, for the following reasons:

(1) If we assume that the above two components exist between the spectra of  $\text{Rb}^*\text{He}_3$  and  $\text{Rb}^*\text{He}_{n_{\max}}$ , the wave number interval between neighboring spectral peaks becomes nearly equal. This agrees with a theoretical result that the interval of the peak positions is approximately equal for different  $n$  as far as  $n \leq n_{\max} (=6)$ .

(2) The theoretical suggestion that  $n_{\max}=6$  indicates the existence of two components.

(3) It is probable that the wave number at peak of the theoretical spectrum of  $\text{Rb}^*\text{He}_{n_{\max}}$  deviates toward red from the observed, as seen for the component of  $\text{Rb}^*\text{He}_3$ . To minimize this deviation, the condition  $n_{\max}=6$  gives the best result.

Thus, we finally conclude that the components at  $9000 \text{ cm}^{-1}$ ,  $8100 \text{ cm}^{-1}$ , and  $7300 \text{ cm}^{-1}$  are from  $\text{Rb}^*\text{He}_4$ ,  $\text{Rb}^*\text{He}_5$ , and  $\text{Rb}^*\text{He}_6$  ( $n_{\max}=6$ ), respectively.

In order to know the peak position and width of each component of spectra, we fitted to the observed spectra superpositions of six spectral components: three Gaussian curves for  $n=3-5$  and three experimentally determined profiles for  $n=1,2,6$ . For  $n=1$ , the profile observed at 50 K was used. The profile for  $n=2$  was obtained by subtracting the spectrum at 50 K from that at 5 K in the case of the  $D_2$  excitation. For  $n=6$ , the profile at 5 K for the  $D_2$  excitation was used. The fitting parameters were the wave numbers at center and FWHMs of the three Gaussian functions, and the relative intensities of the six components ( $n=1-6$ ) of each spectrum. Figure 9 shows an example of the best-fitted curve, together with the resulting three Gaussian curves for  $n=3-5$  and the profiles for  $n=1,2,6$  used in the fitting. The

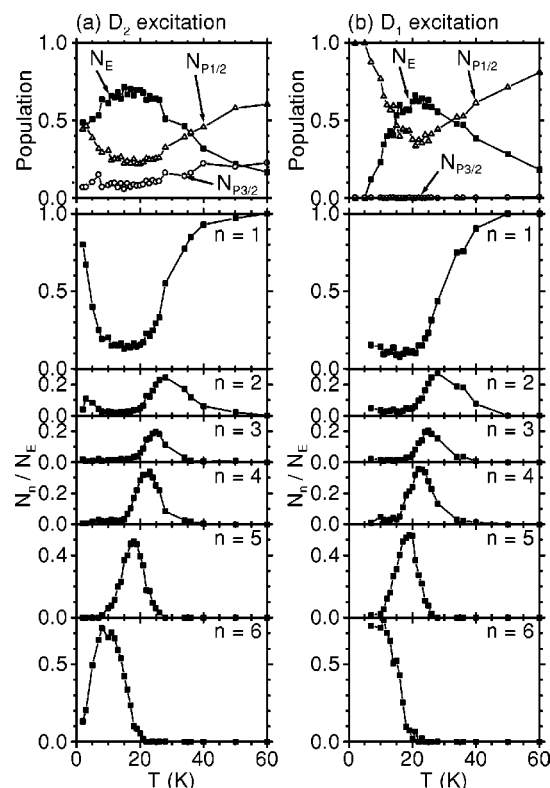


FIG. 10. Populations as functions of  $T$  in the cases of the  $D_2$  excitation (a) and  $D_1$  excitation (b). The  $N_n$  ( $n=1-6$ ) is the relative population of  $\text{Rb}^*\text{He}_n$ , and  $N_{P3/2}$  and  $N_{P1/2}$  are those of  $\text{Rb}(5^2P_{3/2})$  and  $\text{Rb}(5^2P_{1/2})$ , respectively. The  $N_n$  has been normalized by the total population  $N_E (= \sum_{n=1}^6 N_n)$  of  $\text{Rb}^*\text{He}_n$ .

obtained wave numbers at center and FWHMs are  $9949 \text{ cm}^{-1}$  and  $836 \text{ cm}^{-1}$  for  $n=3$ ;  $9105 \text{ cm}^{-1}$  and  $1278 \text{ cm}^{-1}$  for  $n=4$ ; and  $8065 \text{ cm}^{-1}$  and  $1398 \text{ cm}^{-1}$  for  $n=5$ .

The discrepancy between the experimental and theoretical wave numbers at peak becomes larger as  $n$  increases from 1 to 6. We consider that this is due to the accumulation of error in the theoretical calculation with the increase of  $n$ .

### C. Temperature dependence

The  $T$  dependence of the observed spectra shown in Figs. 7(a) and 7(b) is understood as the  $T$  dependence of relative populations of  $\text{Rb}^*\text{He}_n$  ( $n=1-6$ ). We will write the relative populations of  $\text{Rb}^*\text{He}_n$  as  $N_n$  ( $n=1-6$ ), and those of  $\text{Rb}(5^2P_{3/2})$  and  $\text{Rb}(5^2P_{1/2})$  as  $N_{P3/2}$  and  $N_{P1/2}$ . We estimated these populations from the relative intensities of the six spectral components determined by the fitting and of the atomic  $D$  lines, taking into account the  $\nu^3$  dependence of radiative decay rate. With respect to the radiative decay rate  $A_n$  of  $\text{Rb}^*\text{He}_n$  ( $n=1-6$ ), the electric dipole transition moment of  $\text{Rb}-\text{He}_n$  was assumed to be equal to that of the  $\text{Rb } 5^2P-5^2S$  transition.

Figures 10(a) and 10(b) show the obtained relative populations as functions of  $T$ , in the cases of the  $D_2$  and  $D_1$  excitations, respectively. Note that each population  $N_n$  ( $n=1-6$ ) is normalized by the total population of exciplexes,



$N_E = \sum_{n=1}^6 N_n$ . In the case of the  $D_2$  excitation,  $N_E$  has a maximum of about 0.7 around 15 K. On the other hand, in the case of the  $D_1$  excitation,  $N_E$  increases from zero as  $T$  rises above 5 K, and has a maximum of about 0.65 around 21 K. As  $T$  increases above 21 K, it falls in the same way as in the case of the  $D_2$  excitation. In the temperature range  $T > 5$  K where the emission from  $\text{Rb}^*\text{He}_n$  could be observed in both cases of the  $D_2$  and  $D_1$  excitations, temperature dependence of the ratios  $N_n/N_E$  ( $n=1-6$ ) is about the same for both cases. This is because, even in the case of the  $D_2$  excitation, most excimers  $\text{Rb}^*\text{He}$  produced in the  $A^2\Pi_{3/2}$  state relax to the  $A^2\Pi_{1/2}$  before emitting fluorescence or producing  $\text{Rb}^*\text{He}_2$  (at  $T \geq 2$  K), and hence there is no difference in the successive formation process from the case of the  $D_1$  excitation.

At  $T \leq 10$  K, the populations of  $n=1,2,6$  are dominant, and the populations of  $n=3-5$  are negligibly small. The ratio  $N_6/N_E$  greatly increases with increasing  $T$  above 2 K, until it becomes about 0.7 at around 10 K. This high ratio indicates the accumulation of the population of the terminal exciplex  $\text{Rb}^*\text{He}_{n_{\max}}$  ( $n_{\max}=6$ ). As  $T$  increases above 10 K, the populations of  $n=5,4$ , and 3 begin to increase in this order, and the population shifts gradually from  $n=6$  to  $n=1$ . This corresponds to the observed peak shift of the broad spectrum. When  $T$  rises above 40 K,  $N_1$  ( $\approx N_E$ ) decreases rapidly.

We estimate here rate coefficient  $R_n$  for the formation process  $\text{Rb}^*\text{He}_{n-1} \rightarrow \text{Rb}^*\text{He}_n$ , by substituting the obtained values of the relative populations into rate equations in steady state. We consider a temperature range of  $T \leq 15$  K and assume that the dissociation processes  $\text{Rb}^*\text{He}_n \rightarrow \text{Rb}^*\text{He}_{n-1}$  ( $n=1-3$ ) are negligible in this temperature range. Then, the rate coefficients for  $n=1-3$  can be expressed as

$$R_n = \frac{\sum_{k=n}^6 N_k A_k}{N_{n-1}}, \quad (1)$$

where  $N_0$  (for  $n=1$ ) corresponds to the population of the  $\text{Rb}-5^2P$  states. The  $N_0$  for the  $D_2$  excitation case is given by  $N_{P3/2}$ , within the temperature range  $T \leq 5$  K where the formation of  $\text{Rb}^*\text{He}_n$  from  $\text{Rb}(5^2P_{1/2})$  is negligible. Thus, obtained values are  $R_1 \approx 8 \times 10^7 \text{ s}^{-1}$ ,  $R_2 \approx 1 \times 10^7 \text{ s}^{-1}$ , and  $R_3 \approx 4 \times 10^7 \text{ s}^{-1}$ , at 5 K. We see that these values are comparable to radiative decay rates, as expected. (The radiative rate for the atomic  $D_2$  transition is  $3.7 \times 10^7 \text{ s}^{-1}$  [21].) It is noted also that as  $T$  increases from 2 K to about 13 K,  $R_3$  greatly increases from about  $3 \times 10^7 \text{ s}^{-1}$  to  $3 \times 10^8 \text{ s}^{-1}$ .

#### D. Dynamics of the exciplex formation

First, let us consider the decrease of  $N_E$  for the  $D_1$  excitation with decreasing  $T$  below 21 K. This decrease is explained by the existence of the potential barrier ( $26.5 \text{ cm}^{-1}$ ) in the  $A^2\Pi_{1/2}$  state of  $\text{Rb}^*\text{He}$ . Due to the existence of the barrier, the formation of  $\text{Rb}^*\text{He}$  decreases with the decrease of  $T$ . Larger exciplexes  $\text{Rb}^*\text{He}_n$  ( $n=2-6$ ) are produced

through  $\text{Rb}^*\text{He}$ , so that the decrease in the formation of  $\text{Rb}^*\text{He}$  leads to the decrease of  $N_E$ .

Next, we will discuss the experimental fact that the populations of  $n=3-5$  are negligibly small at  $T \leq 10$  K. This indicates that the formation rates  $R_4$ ,  $R_5$ , and  $R_6$  are much larger than  $R_3$ ,  $R_2$ , and  $R_1$ . To understand this difference in the formation rate, let us discuss in the following the formation process  $\text{Rb}^*\text{He}_{n-1} + \text{He} \rightarrow \text{Rb}^*\text{He}_n$  ( $n=2-6$ ) in terms of the potential energy of the system  $\text{Rb}^*\text{He}_{n-1}\text{-He}$ . The interaction between Rb and He is expressed mainly by the van der Waals attraction and the repulsion due to the Pauli exclusion principle. A He atom can approach the Rb core through the region where the Rb valence electron density is small. This simple description gives us a qualitative understanding of the formation process, as described below.

Let us begin with the process  $\text{Rb}^*\text{He} + \text{He} \rightarrow \text{Rb}^*\text{He}_2$ . For both states  $A^2\Pi_{1/2}$  and  $A^2\Pi_{3/2}$  of  $\text{Rb}^*\text{He}$ , the wave function of the  $\text{Rb}^*$  valence electron is well expressed by the spherical harmonics  $Y_1^{\pm 1}$ , where the quantization axis is taken to the molecular axis of  $\text{Rb}^*\text{He}$ . Its density distribution has an “applelike” shape. Therefore, it is possible for the second He atom to approach the Rb core without going over a potential barrier, as long as it comes to the other side of the first He atom.

When the third He atom approaches the Rb core, the situation is different from the case of the second He, because two potential minima are already occupied by the two He atoms. Therefore, we consider that the third He atom has to go over a potential barrier in order to stick to the Rb core. To obtain a quantitative estimation of the barrier, we calculated potential-energy surface for the system  $\text{Rb}^*\text{He}_2\text{-He}$ . It should be mentioned that the barrier becomes higher as the fine-structure splitting  $\Delta$  becomes larger. As mentioned in the introduction, we are thus interested in comparing the result with the potential surface for  $\text{Cs}^*\text{He}_2\text{-He}$ , which is presented in Sec. IV F.

In the calculation, we fixed the  $\text{Rb}^*$  at  $(y,z)=(0,0)$  and the two He atoms of  $\text{Rb}^*\text{He}_2$  at equilibrium positions  $(0, \pm r_0)$  ( $r_0=3.24 \text{ \AA}$ ). The third He atom was located on the  $y$ - $z$  plane, and we will express its position as  $(r \sin \theta, r \cos \theta)$ . As in Sec. II, *ab initio* potential energies of the excited states were calculated at the RHF level [11], and the spin-orbit interaction was taken into account.

Figure 11(a) shows a contour map of the obtained potential-energy surface of the lowest excited state in the region of  $0^\circ \leq \theta \leq 90^\circ$ . As expected, we see that the third He atom has to go over a potential barrier before entering a potential well in the region of  $r \approx r_0$  and  $\theta \geq 45^\circ$ . The saddle point is located at  $r=4.9 \text{ \AA}$  and  $\theta=38^\circ$ , and the energy of the point (maximum energy along the minimum energy path for the formation) is  $20.5 \text{ cm}^{-1}$  above the dissociation limit  $\text{Rb}^*\text{He}_2$  ( $A^2\Pi_{1/2}$ ) + He. As already mentioned, the formation rate  $R_3$  greatly increases as  $T$  increases from 2 K to about 13 K. The existence of the barrier may be the reason for this. The potential well has a minimum at  $r=3.24 \text{ \AA}$  and  $\theta=65^\circ$  with a depth of  $114.4 \text{ cm}^{-1}$  below the saddle point. There exist several bound states in this potential well.

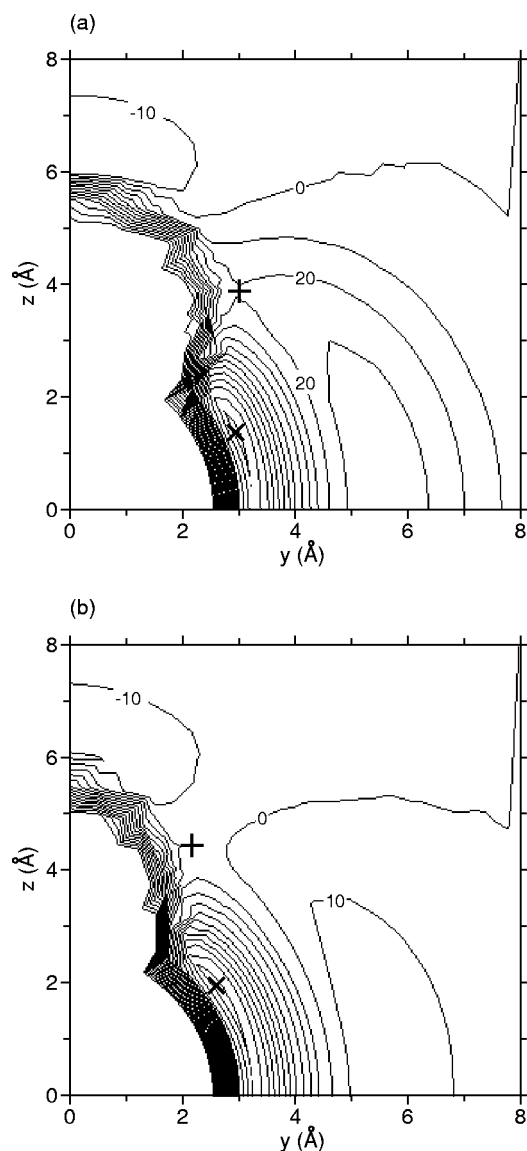


FIG. 11. Potential-energy surfaces calculated for the system  $\text{Rb}^*\text{He}_2\text{-He}$ . The  $\text{Rb}^*$  was fixed at  $(y,z)=(0,0)$  for both (a) and (b). The two He atoms of  $\text{Rb}^*\text{He}_2$  were fixed at  $(0,\pm 3.24)$  in the case of (a), and at  $(0,-3.24)$  and  $(-3.24 \sin 11^\circ, 3.24 \cos 11^\circ)$  in the case of (b) (all in units of Å). The energy is in units of  $\text{cm}^{-1}$  and the zero of energy is at each dissociation limit  $\text{Rb}^*\text{He}_2 + \text{He}$ . The contour interval is  $10 \text{ cm}^{-1}$ . The marks “+” and “x” show the positions of saddle point and potential minimum, respectively.

Up to now we have fixed the two He atoms of  $\text{Rb}^*\text{He}_2$  at their equilibrium positions. During the formation process of  $\text{Rb}^*\text{He}_3$ , however, they can move in the depressions of the applelike density distribution of the Rb valence electron. To estimate this effect on the potential barrier, we considered the vibration in  $\text{Rb}^*\text{He}_2$ . The most important vibrational mode for lowering the potential barrier is the bending vibration, and the one in the  $y$ - $z$  plane under the present configuration of the atoms. We took into account only its zero-point vibration, because the energy needed to excite the vibration,  $\Delta\epsilon_b = 34.5 \text{ cm}^{-1}$ , is large compared with the thermal energy at  $T \lesssim 30 \text{ K}$ . Setting the bending angle to the value corre-

sponding to the classical turning point ( $\angle \text{He-Rb-He} = 169^\circ$ ), we calculated the potential surface for the third He atom on the  $y$ - $z$  plane. The result is shown in Fig. 11(b). The energy of the saddle point is lowered to  $3.4 \text{ cm}^{-1}$  below the dissociation limit  $\text{Rb}^*\text{He}_2$  (bended) + He. The cross section for the formation of  $\text{Rb}^*\text{He}_3$  might, however, be small even in this extreme case, due to the narrow channel in the vicinity of the saddle point.

Now let us consider the reason why  $R_4$ ,  $R_5$ , and  $R_6$  are larger than  $R_3$ , comparing the formation processes of  $\text{Rb}^*\text{He}_3$  and  $\text{Rb}^*\text{He}_n$  ( $n=4-6$ ). A significant difference between  $n=3$  and  $n=4-6$  is the density distribution of the Rb valence electron of the preceding exciplexes  $\text{Rb}^*\text{He}_2$  and  $\text{Rb}^*\text{He}_n$  ( $n=3-5$ ). As already mentioned in Sec. II, the density distribution for  $\text{Rb}^*\text{He}_n$  ( $n=3-5$ ) is well expressed by that of the  $p_x$  orbital, under the condition that the  $n$  He atoms are located on the  $y$ - $z$  plane and on a circle with the center at the position of Rb. The “dumbbell-like” density distribution presents around its neck a potential well for He atoms. According to the pair potential of  $\text{Rb}^*\text{-He}$  calculated in Sec. II, the depth of the potential minimum for the  $p_x$  orbital is  $176.8 \text{ cm}^{-1}$ . Even at low temperatures, He atoms are energetically allowed to approach this potential well through the nodal  $y$ - $z$  plane of the  $p_x$  orbital. This is in contrast to the formation of  $\text{Rb}^*\text{He}_3$  described above. The rearrangement of He atoms would proceed more easily than in the case of the formation of  $\text{Rb}^*\text{He}_3$ , because He atoms in the potential well can move along the circle more freely than those in the depressions of the applelike density distribution for  $\text{Rb}^*\text{He}_2$ . Furthermore, the number of vibrational modes of the preceding exciplex  $\text{Rb}^*\text{He}_{n-1}$  increases with increasing  $n$ . This is favorable for the efficient release of the translation and binding energies between  $\text{Rb}^*\text{He}_{n-1}$  and He, during the formation process of  $\text{Rb}^*\text{He}_n$ .

Finally, let us consider the experimental fact that the population shifts from  $n=6$  to  $n=1$ , as  $T$  increases from 10 K to about 40 K. In this temperature range, the thermal energy is of the same order of magnitude as the energy difference  $\Delta E_n$  (see Sec. II), which gives the energy required to dissociate a He atom of  $\text{Rb}^*\text{He}_n$  from the Rb core. As a result, the rate for collision-induced dissociation process  $\text{Rb}^*\text{He}_n + \text{He} \rightarrow \text{Rb}^*\text{He}_{n-1} + \text{He} + \text{He}$  rises as  $T$  increases. In addition, the rate for the formation process  $\text{Rb}^*\text{He}_{n-1} + \text{He} \rightarrow \text{Rb}^*\text{He}_n$  falls with the increase of  $T$ , because the kinetic energy of translation between  $\text{Rb}^*\text{He}_{n-1}$  and He can be used to dissociate any one of the  $n-1$  He atoms from the Rb core. Such a temperature dependence of the dissociation and formation rates explains the fact that the population shifts from  $n$  to  $n-1$  with increasing  $T$ . This discussion applies also to the case of  $n=1$ : the calculated binding energy of  $\text{Rb}^*\text{He}$  (see Table I), which corresponds to the energy  $\Delta E_1$ , explains the decrease of  $N_1$  with increasing  $T$  above 40 K. We believe that  $\text{Rb}^*\text{He}_7$  should hardly be populated, even when  $T$  increases from about 10 K and the thermal energy becomes comparable to  $-\Delta E_7$  (see Fig. 3). Under this situation, the thermal energy becomes also comparable to  $\Delta E_6$ , which results in the decrease of  $N_6$ . As a result, the production of

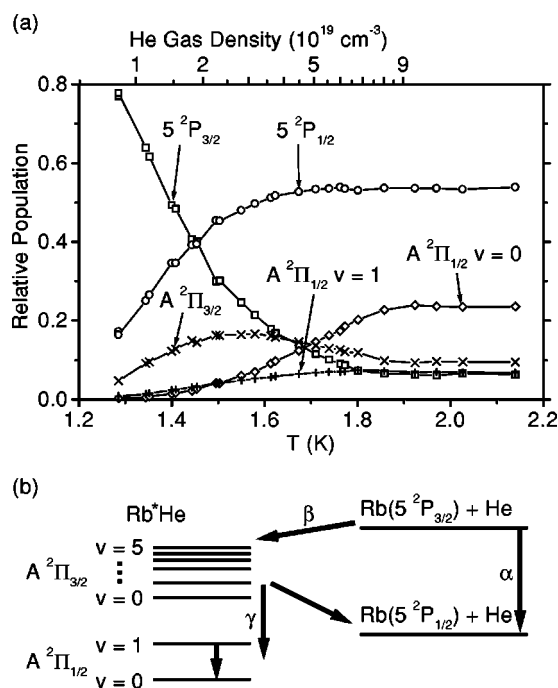


FIG. 12. (a) Relative populations of the vibrational levels of  $Rb^*He$  and the  $5^2P$  states of Rb, in the case of the  $D_2$  excitation. As for the  $A^2\Pi_{3/2}$  state of  $Rb^*He$ , the total population of the four vibrational levels ( $0 \leq v \leq 3$ ) is shown. (b) Relaxation processes in the excited states after the  $D_2$  excitation of Rb. With respect to the three processes labeled by  $\alpha$ ,  $\beta$ , and  $\gamma$ , the rate coefficients were estimated (see text).

$Rb^*He_7$  is also suppressed, since  $Rb^*He_7$  is created via  $Rb^*He_6$ .

### E. He gas density dependence

As already mentioned, in the case of the  $D_2$  excitation, the temperature dependence of the spectra of  $Rb^*He$  at  $T < T_c$  ( $= 1.9$  K) (see Fig. 8) is caused mainly by a change of the He gas density [see Fig. 5(b)]. The He gas density dependence of the spectra is due to a change in the population distribution over the vibrational levels of  $Rb^*He$ . In order to obtain the populations, we fitted to each spectrum a superposition of the atomic  $D_2$  and  $D_1$  lines and the theoretical emission spectra from the vibrational states of  $Rb^*He$  shown in Fig. 2. The fitting parameters were the relative populations of the  $5^2P_{3/2}$  and  $5^2P_{1/2}$  states of Rb and those of the vibrational states of  $Rb^*He$ . The states  $A^2\Pi_{3/2} v=4,5$  of  $Rb^*He$  were not taken into consideration: the wave number difference between the main peak of each theoretical spectrum and the center of the  $D_2$  line was smaller than the spectral resolution of the detection system ( $\approx 20 \text{ cm}^{-1}$ ), and hence it was impossible to distinguish each spectrum from the  $D_2$  line. The best-fitted curves are shown by dotted lines in Fig. 8, where we see that they are in good agreement with the observed spectra.

Figure 12(a) shows the obtained relative populations. As for the  $A^2\Pi_{3/2}$  state of  $Rb^*He$ , the intensity of the spectral component from each vibrational level is weak, so that the relative population of each level is small ( $< 0.07$ ) and has

ambiguity. Therefore, only the total population of the  $A^2\Pi_{3/2}$  state is shown in Fig. 12(a). We see that, as the He gas density increases, (1) the population of  $Rb(5^2P_{1/2})$  increases relatively to that of  $Rb(5^2P_{3/2})$ , (2) the total population of  $Rb^*He$  increases relatively to that of the  $Rb-5^2P$  states, (3) the total population of  $Rb^*He(A^2\Pi_{1/2})$  increases relatively to that of  $Rb^*He(A^2\Pi_{3/2})$ , and (4) the population of the  $A^2\Pi_{1/2} v=0$  state increases relatively to that of the  $A^2\Pi_{1/2} v=1$ . All of these are explained by the increase in the rates of collision-induced relaxation processes, which are shown by arrows in Fig. 12(b).

The fact that population is distributed over various states indicates that the relaxation rates are comparable to the radiative decay rate. We estimated the rate coefficients for the following three processes:  $\alpha$ , for the fine-structure relaxation of  $Rb(5^2P_{3/2} \rightarrow 5^2P_{1/2})$ ;  $\beta$ , for the formation of  $Rb^*He$  [ $Rb(5^2P_{3/2}) + He \rightarrow Rb^*He(A^2\Pi_{3/2})$ ]; and  $\gamma$ , for the fine-structure relaxation of  $Rb^*He$  ( $A^2\Pi_{3/2} \rightarrow A^2\Pi_{1/2}$ ) [see Fig. 12(b)]. We considered the total populations of the states  $A^2\Pi_{3/2}$  and  $A^2\Pi_{1/2}$ , respectively, neglecting vibrational structures. We substituted the values of the relative populations into rate equations in steady state obtained under the following assumptions.

(1)  $Rb^*He(A^2\Pi_{1/2})$  is not produced directly from  $Rb(5^2P_{3/2}) + He$ , but produced through  $Rb^*He(A^2\Pi_{3/2})$ . This assumption is derived from the experimental fact that the total population of  $Rb^*He(A^2\Pi_{1/2})$  is negligibly small, in spite of the large population of  $Rb(5^2P_{3/2})$  at  $T \leq 1.4$  K.

(2) Formation of  $Rb^*He_n$  ( $n=2-6$ ) from  $Rb^*He$  is negligible. This is based on the fact that with respect to the spectrum at 2 K in Fig. 7(a), the integrated intensity of emission from  $Rb^*He_n$  ( $n=2-6$ ) is less than 4% of the total emission intensity.

(3) Any collisional excitation process is negligible in the temperature range  $T < 2.1$  K.

We took into account also the experimental fact that  $Rb(5^2P_{1/2})$  did not produce  $Rb^*He$  at  $T < 5$  K. Finally we obtained  $\alpha \leq 6.9A$ ,  $4.4A \leq \beta \leq 11A$ , and  $\gamma \approx 1.9A$  at 1.80 K, where  $A$  ( $= 3.7 \times 10^7 \text{ s}^{-1}$ ) is the radiative decay rate for the  $Rb D_2$  transition.

The fine-structure changing process in cold and dense He has not been well investigated so far. Gallagher investigated the cross sections for the fine-structure changing of an alkali-metal atom ( $^2P_{3/2} \rightarrow ^2P_{1/2}$ ) due to the binary collisions with a rare-gas atom at the temperature higher than a room temperature [26]. The extrapolation of his results to a low temperature suggests that  $\alpha$  should be several orders of magnitude smaller than  $A$  when only the binary collisions are considered. Namely, the population ratio of  $Rb(5^2P_{1/2})$  to  $Rb(5^2P_{3/2})$  obtained in our experiment is much larger than that expected from above extrapolation. This discrepancy may suggest that there exists indirect fine-structure changing process through formation and dissociation of  $Rb^*He$ , occurring only at a low temperature in high density He. The rate coefficient  $\gamma$  may also be increased by the similar process through the formation and dissociation of  $Rb^*He_2$ .

### F. Differences between Rb and Cs

Let us compare the results of the present work and our previous experiment with Cs, which was recently reported



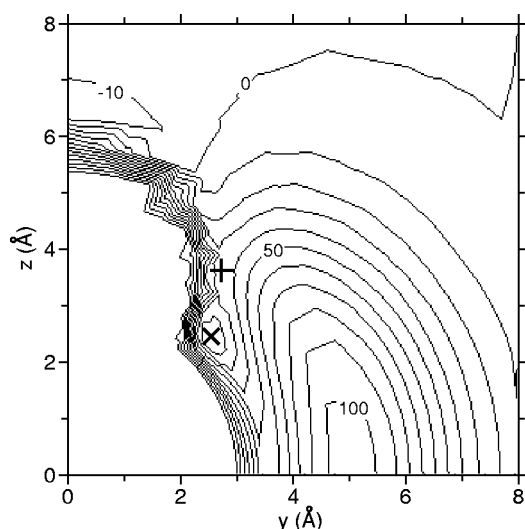


FIG. 13. Potential-energy surface calculated for the system  $\text{Cs}^*\text{He}_2\text{-He}$ . The  $\text{Cs}^*$  atom was fixed at  $(y,z)=(0,0)$  and the two He atoms of  $\text{Cs}^*\text{He}_2$  were fixed at  $(0,\pm 3.5)$ , in units of Å. The energy is in units of  $\text{cm}^{-1}$  and the zero of energy is at the dissociation limit  $\text{Cs}^*\text{He}_2$  ( $A^2\Pi_{1/2}$ ) + He. The contour interval is  $10 \text{ cm}^{-1}$ . The marks “+” and “x” show the positions of saddle point and potential minimum, respectively.

[9]. The Cs cell used in the previous experiment contained about the same amount of He as the present work. The important point to understand the difference between the results for Rb and Cs is that the fine-structure splitting of the  $\text{Cs-}6^2P$  states ( $\Delta=554.0 \text{ cm}^{-1}$ ) is larger than that of the  $\text{Rb-}5^2P$  states ( $\Delta=237.6 \text{ cm}^{-1}$ ).

First, it has been found that  $n_{\max}$  is 6 for Rb and 2 for Cs. To compare the formation processes of  $\text{Rb}^*\text{He}_3$  and  $\text{Cs}^*\text{He}_3$ , numerical calculation of the potential-energy surface was carried out for the system  $\text{Cs}^*\text{He}_2\text{-He}$ . As in the calculation for  $\text{Rb}^*\text{He}_2\text{-He}$  (see Sec. IV D), we fixed the  $\text{Cs}^*$  at  $(y,z)=(0,0)$  and the two He atoms of  $\text{Cs}^*\text{He}_2$  at equilibrium positions  $(0,\pm r_0)$  ( $r_0=3.5 \text{ Å}$ ). We calculated the potential energy of the system by summing over all pair interactions, and took into account the spin-orbit interaction of the  $\text{Cs-}6^2P$  states. We used potential energies calculated by Pascale [10] for the  $\text{Cs}^*\text{-He}$  interactions, and the analytical Hartree-Fock-dispersion individual-damping form of the pair potential of Aziz and Slaman [27] for the He-He interactions. Figure 13 shows the potential-energy surface obtained for the lowest excited state. Due to the larger splitting  $\Delta$ , the potential barrier is higher than that for  $\text{Rb}^*\text{He}_2\text{-He}$ . The saddle point is located at  $r=4.5 \text{ Å}$  and  $\theta=37^\circ$ , and the energy of the point is  $33.1 \text{ cm}^{-1}$  above the dissociation limit  $\text{Cs}^*\text{He}_2$  ( $A^2\Pi_{1/2}$ ) + He. The larger value of the splitting results in also the narrower and shallower potential well which has a minimum at  $r=3.5 \text{ Å}$  and  $\theta=46^\circ$  with a depth of  $22.4 \text{ cm}^{-1}$  below the saddle point. It should be noted that there exists no vibrational state in this well. As in Sec. IV D, we considered the bending vibration in  $\text{Cs}^*\text{He}_2$  ( $\Delta\epsilon_b=26.2 \text{ cm}^{-1}$ ), setting the bending angle to the value of the classical turning point for the zero-point vibration ( $\angle \text{He-Cs-He}=167^\circ$ ). The energy of the saddle point is low-

ered to  $7.6 \text{ cm}^{-1}$  above the dissociation limit  $\text{Cs}^*\text{He}_2$  (bended) + He. Nevertheless, there still does not exist a vibrational state in the well. We consider that the absence of the vibrational state prevents the formation of  $\text{Cs}^*\text{He}_3$ . As already mentioned, the potential well has several bound states in the case of Rb. This difference explains well why  $n_{\max}=2$  for Cs, while  $n_{\max}>2$  for Rb.

Second, in the case of the  $D_1$  excitation, the integrated intensity of emission from  $\text{Rb}^*\text{He}_n$  ( $n=1-6$ ) accounted for about 50% of the total emission intensity at  $T\approx 25 \text{ K}$ , whereas the emission from  $\text{Cs}^*\text{He}_n$  ( $n=1,2$ ) was only about 1% at maximum. This is because the potential barrier in the  $A^2\Pi_{1/2}$  state of  $\text{Cs}^*\text{He}$  ( $75.2 \text{ cm}^{-1}$ ) [9] is higher than that of  $\text{Rb}^*\text{He}$  ( $26.5 \text{ cm}^{-1}$ ), due to the larger splitting  $\Delta$ .

A similar effect of the potential barrier in the  $A^2\Pi_{1/2}$  state was indicated by experiments with He droplets [28]. With respect to the  $D_1$  excitation of alkali atoms on He droplets, the photoinduced desorption of  $\text{K}^*\text{He}$  took place more slowly than that of  $\text{Na}^*\text{He}$  [28], and emission from  $\text{Rb}^*\text{He}$  was not observed [6]. These were explained by the existence of a similar potential barrier in the  $A^2\Pi_{1/2}$  state.

Finally, we estimated the three relaxation rate coefficients  $\alpha$ ,  $\beta$ , and  $\gamma$  in the case of Cs, using the same method as described in Sec. IV E. The  $A^2\Pi_{1/2}v=0$  state of  $\text{Cs}^*\text{He}$  is a quasibound state, so we took into consideration also the predissociation process  $\text{Cs}^*\text{He}$  ( $A^2\Pi_{1/2}$ )  $\rightarrow$   $\text{Cs}(6^2P_{1/2})$  + He [9], which was not considered in the case of Rb. From the emission spectrum observed at  $1.81 \text{ K}$  for the  $D_2$  excitation of Cs, we obtained  $\alpha\lesssim 2.0A'$ ,  $16A'\lesssim\beta\lesssim 18A'$ , and  $0.58A'\lesssim\gamma\lesssim 0.76A'$ , where  $A' (=3.7\times 10^7 \text{ s}^{-1})$  is the radiative decay rate for the Cs  $D_2$  transition ( $6^2P_{3/2}\rightarrow 6^2S_{1/2}$ ) [21]. The rate coefficient  $\gamma$  for the fine-structure relaxation of  $\text{Cs}^*\text{He}$  is less than half of that of  $\text{Rb}^*\text{He}$ . This is qualitatively consistent with a prediction derived from the adiabaticity parameter [29], which tells us that the probability of nonadiabatic transition decreases with an increase in the transition energy (roughly expressed by  $\Delta$  in the present case).

## V. CONCLUSION

We have reported on the emission spectra of  $\text{Rb}^*\text{He}_n$  observed when Rb atoms were excited to the  $5^2P$  states in a cryogenic  $^4\text{He}$  gas. By observing the spectra at various temperatures ( $T\leq 100 \text{ K}$ ) and with the help of *ab initio* potential calculation, we have assigned the spectra of all of  $\text{Rb}^*\text{He}_n$  ( $n=1-6$ ). We have found that the emission spectrum of the exciplex in liquid He agrees with that of  $\text{Rb}^*\text{He}_6$ , and this is consistent with our theoretical result that the vibrational ground state of  $\text{Rb}^*\text{He}_6$  has the lowest-energy level among all  $n$ .

From the spectral profiles, the relative population for each  $n$  and the exciplex formation rate coefficient  $R_n$  for  $\text{Rb}^*\text{He}_{n-1} + \text{He} \rightarrow \text{Rb}^*\text{He}_n$  have been estimated. Especially, we have paid attention to the process of  $\text{Rb}^*\text{He}_2 + \text{He} \rightarrow \text{Rb}^*\text{He}_3$ , since  $R_3$  depends strongly on the temperature between  $2 \text{ K}$  and  $13 \text{ K}$ . We have calculated the potential-energy surface for the system  $\text{Rb}^*\text{He}_2\text{-He}$ , and have found that the strong temperature dependence of  $R_3$  is considered



to be due to a potential barrier in this formation process, which originates from the spin-orbit coupling. By performing similar calculation for the system  $\text{Cs}^*\text{He}_2\text{-He}$  which has a larger spin-orbit coupling strength, we have found that there is no bound state under the assumption that the bending angle of  $\text{Cs}^*\text{He}_2$  is within the range of the zero-point bending vibration. This can explain well the experimental fact that  $\text{Cs}^*\text{He}_3$  is not produced [9].

At  $T < T_c (= 1.9 \text{ K})$ , where the He gas density in the cell varies, we observed also vibrational structure in the emission spectra of  $\text{Rb}^*\text{He}$ , which was strongly dependent on the He gas density. We have obtained the population for the vibrational states of the  $A^2\Pi_{1/2}$  and  $A^2\Pi_{3/2}$  states, and estimated the rate coefficient for the fine-structure changing process of  $\text{Rb}^*\text{He}$ . This rate coefficient has also been estimated for  $\text{Cs}^*\text{He}$ .

Through a comparison with our previous work with Cs [9], it has become clear that the spin-orbit interaction plays an important role in alkali-atom- $\text{He}_n$  exciplex formation. For example, potential barriers originating from the spin-orbit coupling make difference in  $n_{\max}$  between Rb and Cs, and prevent exciplex formation after the  $D_1$  excitation at  $T < 10 \text{ K}$  for Rb and at any temperature for Cs. As an alkali-

metal atom becomes smaller, the fine-structure splitting  $\Delta$  of the first  $P$  states becomes smaller, and thus its contribution to the potential energy becomes smaller. Therefore, experiments with K ( $\Delta = 57.7 \text{ cm}^{-1}$ ) and Na ( $\Delta = 17.2 \text{ cm}^{-1}$ ), now underway in our laboratory, will help to understand further the effects of the spin-orbit interaction.

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